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STUDIES IN THE CLARIFICATION OF UNFERMENTED FRUIT JUICES.

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PURPOSE AND SCOPE OF THE INVESTIGATION.

When an unfermented fruit juice, such as that of apples or grapes, is prepared and preserved by the methods ordinarily employed, a more or less copious precipitate consisting of cellular débris and heat-coagulable material is formed after pasteurization. This fact is responsible for the usual practice of pasteurization and storage, followed after an interval by transfer to the final containers and a second pasteurization. Even when the formation of a coagulum in the final container is thus prevented, the liquid remains permanently turbid and opaque from the presence of considerable quantities of suspended colloidal materials, which are unaffected by heating and subsequent storage. In the case of a few heavily pigmented varieties of grapes, such as the Ives, Concord, Clevener, and other purple varieties, the intense coloration of the juices masks their turbidity and renders them attractive to the eye. In most grape varieties, however, the juices obtained are densely opaque, tawny yellow, or

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brownish colloidal suspensions, distinctly uninviting in appearance. While a considerable number of these juices are superior in flavor and in beverage quality to juices of the Concord type, their appearance counts so heavily against them that, with the exception of Catawba, no systematic attempts have been made to place them on the market, and they seem to be very little used for juice making even in districts in which the production of such varieties is in excess of market demands for fresh grapes.

Unfermented apple juice, or "sweet cider," is to a very large extent a seasonal product, made and consumed in large quantities during the autumn months, but practically unobtainable at other seasons. Pasteurized unfermented cider has not gained greatly in popularity, its consumption in recent years having entirely failed to keep pace with the increase in consumption of synthetic soft drinks. While this failure to gain in favor has been due in considerable part to lack of uniformity in the character and quality of the product and to loss of distinctive flavor or development of foreign flavors as a result of faulty preparation, the criticism most frequently heard is that pasteurized ciders are "muddy" and unattractive looking on account of the presence of suspended matter. In view of the reception given the clear, attractive juices placed on the market by a few manufacturers employing zealously guarded special methods of preparation, it seems certain that a very considerable increase in demand and consumption as well as a very large extension of the small-scale home manufacture of unfermented juices would result if simple, effective methods of making brilliant, transparent juices of unaltered beverage quality were generally available.

One of the purposes of the studies of fruit juices which have been in progress in the Bureau of Plant Industry for the last three years is the development of simple, generally available methods for the preparation of unfermented fruit-juice beverages, by which the fruit grower or the individual consumer may make products of good quality, distinctive flavor, and attractive appearance without the use of special equipment. Concurrently a large number of varieties of apples and grapes have been studied with reference to their special fitness for the making of various products. It has consequently been possible to employ in the work each year samples of juices from approximately 250 varieties of apples and more than 60 varieties of grapes, including nearly all the more widely distributed varieties of these fruits. Materials of the greatest possible diversity have been available for study, affording an unusual opportunity for testing the general applicability of proposed methods.

At the outset the devising of satisfactory methods of clarification was recognized as a very important part of the problem, requiring entrance into a very imperfectly known portion of the field of colloid

chemistry. It is known that the specific flavor of a fruit juice is determined in part by the ratio borne by one of the colloids (tannin) to the acid and sugar content and in part by very imperfectly known and complex constituents which are probably in the colloidal condition. While many of the pigments which give juices their color are crystalline substances, others are either colloids or closely associated with colloids. In order that a juice may be clarified without reducing its value as a beverage, these constituents must remain unaltered by the treatment, which must at the same time completely remove from the liquid other colloids, including pectins, gums, complex carbohydrates, and nitrogenous bodies. The methods which may be employed to make such a separation are greatly restricted by the conditions, and the preservation of desirable constituents is more difficult than the removal of the undesirable ones. This is especially the case in devising methods which the small producer without special equipment can use.

For these reasons, the literature dealing, both from the theoretical and from the practical point of view, with the clarification of such colloidal solutions as are encountered in brewing, wine making, and sugar manufacture was examined for suggestions as to possible lines of attack, and considerable time was spent in determining the applicability to the problem in hand of methods used in these industries. No attempt to review this enormous literature will be made, but it may be of interest to state the unsatisfactory or negative results obtained in attempts to utilize some of these methods before describing the method found most effective.

METHODS OF CLARIFICATION GENERALLY EMPLOYED.

The methods of clarification employed by wine makers and brewers and in sugar manufacture may be grouped broadly into three classes: (1) Those in which the colloid is destroyed by the use of enzyms; (2) those which bring about by chemical treatment the formation of a precipitate which "envelops" and carries down suspended material; and (3) those in which the colloid is removed by adsorption upon insoluble, chemically inert adsorbing agents.

CLARIFICATION BY MEANS OF ENZYMS.

The Wallerstein (*10*, *27*, *28*, *29*)[1] process for the prevention of the development of cloudiness, or "haze," in bottled beer when placed upon ice prior to serving is an instance of the first treatment. According to the results of Brown's extended investigations (*4*), the appearance of "haze" under such conditions is due to the presence in

[1] Serial numbers (italic) in parentheses refer to "Literature cited" at the end of this bulletin.

the finished beer of a reversible colloid formed by combination of hop tannin with a protein of the wort. The solubility of this colloid is decreased by cooling the liquid, with the result that turbidity appears at low temperatures but disappears again on warming. In the Wallerstein process (*10*, p. 605–607; *27*, *28*, *29*) a proteolytic enzym, which can be either pepsin, papain, or bromelin, is added to the beer at the end of the main fermentation in amounts of 1 to 2 grams per hundred liters. The protein-tannin compound is attacked and converted into simpler completely soluble products by the enzym, with the result that the beer remains clear irrespective of the temperatures to which it may later be subjected.

Because of the number and diverse character of the constituents which it is desirable to remove, as well as the character of those which must be preserved, it appeared inherently improbable that enzyms could be successfully employed in the clarification of apple or grape juice or that, even if such a process could be developed, it could be made of such character as to be generally usable. Inasmuch as no indication could be found in the literature that any investigation into the possibilities had been made, some work was begun in 1918. It is still in progress and will be reported elsewhere. It has been possible under laboratory conditions to obtain satisfactory clarification combined with the preservation of the characteristic flavors of juices by the use of enzyms, but the method has not as yet been sufficiently simplified to meet the need for a method requiring no special technical skill and usable on any scale.

French cider makers lay much stress upon the coagulation of the pectins of apple must immediately after pressing as an essential step in the making of high-grade clear ciders. Warcollier (*30*) recommends that juices be held at 4° or 5° C. until the pectase present has coagulated the pectins which collect at the surface to form the "chapeau," or "head," and the settlement of cellular débris and dirt to the bottom has occurred. He suggests that elimination of most of the undesirable organisms which might injuriously affect the subsequent fermentation will thereby be effected. He states that the juice will be perfectly limpid and clear if the conditions be made such that fermentation be prevented during the period of defecation. Arnou (*3*, p. 80–84) devotes a considerable section of his work to the subject, stating that the permissible range of temperature is from 6° to 12° C. and the time required from 12 to 24 hours. In case the juice is deficient in pectase, Arnou suggests the use of sodium or potassium carbonate, calcium sulphate, potassium metabisulphite, or sodium chlorid, and quotes Warcollier as advocating the use of 80 grams of tartaric acid and 30 grams of calcium carbonate per hectoliter of juice to hasten coagulation. He also remarks that apples from differ-

ent districts of France (hence presumably of different varieties) show differences in the readiness with which coagulation of the pectins is obtained, that neither green nor overripe fruits give satisfactory results, that juices low in acid and tannin content coagulate readily, and that successful coagulation is obtained only when fermentation is prevented during the period of defecation.

It has been impossible in the laboratory of the Bureau of Plant Industry to produce such results as are described by these authors without having recourse to some of the chemical treatments which they suggest. At a temperature of 4° C. pectase is inactivated or acts so slowly as to fail entirely to bring about coagulation of the pectins. At higher temperatures alcoholic fermentation is not prevented and usually proceeds so rapidly as soon to make it impossible to classify the juice as unfermented. It is possible to produce almost instantaneous coagulation of pectins by some of the chemical treatments outlined by the French writers cited, but such treatments are not to be recommended, for the reason that their employment seriously detracts from the beverage quality of the juice.

CLARIFICATION BY THE FORMATION OF A PRECIPITATE.

Various methods of clarification employed in wine making and vinegar making may be grouped together, since they all depend upon the production in the liquid of a voluminous precipitate, which gradually subsides, carrying down with it the particles causing turbidity. A rather careful study of such methods indicates that none of them can be expected to give satisfactory results with unfermented juices. The method of clarifying wines most widely employed by European wine makers and most fully discussed in works on wine making is precipitation by the addition of tannin and gelatin. Since the precipitate is the product of a definite chemical reaction, perfect results are obtainable only when the quantities of the reagents are exactly adjusted, a slight excess of gelatin forming a stable colloidal suspension. But tannin is present in every fruit juice (its quantity showing wide differences with varieties and considerable differences in a single variety when grown in different years or under differing cultural and environmental conditions), and this tannin enters into the reaction with gelatin. For this reason the amounts of tannin and gelatin to be employed must be determined by experiment for every juice, and with such viscous materials as grape and apple juices the outcome of such experiments can be certainly determined only after some days. This alone makes the method impracticable. The further fact that the tannin of a juice plays an essential rôle in determining its characteristic flavor and that its removal results in marked alteration of flavor makes the

method useless for fruit juices. The same objections apply to the use of such materials as fish glue, egg albumen, milk, casein, and blood; the precipitation obtained with these substances is due to reaction with tannin or the acids present, or both, with consequent alteration of flavor.

As the work of La Marca (*16*) upon the effects of clarifying agents on the chemical composition of wines has shown, perceptible alteration in flavor as well as in chemical composition of the wine results from the employment of such materials, which led La Marca to advise strongly against their use by wine makers.

A rather careful study carried on in the laboratory of the Bureau of Plant Industry has yielded results showing conclusively that the use of any of the nitrogenous materials previously mentioned as a clarifying agent for unfermented fruit juices is highly inadvisable. The viscosity of most juices is sufficiently high to make the subsidence of the precipitate extremely slow and incomplete. All the substances used are complex protein mixtures containing constituents which are to some degree soluble in the juice, and the introduction of such sources of nitrogen makes the liquid a better medium for the growth of molds. The alteration of flavor produced by the loss of tannin and the introduction of foreign material is perceptible in all juices and amounts to denaturation in the case of the more delicately flavored ones. For these reasons the use of such methods with unfermented juices is ineffective and injurious.

CLARIFICATION BY THE USE OF INERT ADSORBING AGENTS.

The third group of methods for clarifying colloidal solutions or suspensions is that employing chemically inert solids as adsorbing agents. Methods of clarifying wine and vinegar and some other liquids by means of such materials as fuller's earth and Spanish clay have been developed empirically and have been in use for long periods, while the use of carbons in decolorizing cane juice has been discussed in the literature, according to Zerban (*34*), since 1785; but it is only very recently that much attention has been devoted to the study of solid adsorbents for clarifying fruit juices.

CARBONS AS CLARIFYING AGENTS FOR FRUIT JUICES.

The studies of solid adsorbents made in the laboratory of the Bureau of Plant Industry began in 1918 with a study of a considerable number of carbons, which included, with others, samples of a number of special filtering carbons supplied by American manufacturers and various samples of purified animal charcoals obtained through chemical supply houses. The work included the treatment of a large number of apple and grape juices, immediately after pressing or after

preliminary pasteurization and sedimentation, with various amounts of each of the carbons, followed by the removal of the carbon and the subsequent examination of the juices with respect to alteration of color and flavor, degree of removal of colloidal matter, and ability to withstand subsequent pasteurization without formation of precipitate. In view of the character of the results, a detailed statement of the experimental work is considered unnecessary, but a somewhat extended statement of the difficulties encountered may be made.

(1) In order to produce anything approaching a satisfactory subsidence of the precipitate after adding carbon it is necessary first to filter the juice, as Gore (*14*) has pointed out. The filtration of freshly pressed apple or grape juices by any of the ordinary methods is practically impossible, and even under high pressure is extremely slow and difficult, as the filter quickly becomes clogged with cellular débris and gummy material. The use of diatomaceous ("infusorial") earth, which Gore has suggested as an aid to this preliminary filtration, increases the rate somewhat, but does not eliminate entirely the clogging and frequent stoppage of filters of any of the usual types. With grape juice expressed after heating the fruit, it is a practical impossibility to make such filtration.

(2) The most marked property of all the carbons examined in the course of the work was their high decolorizing power for both apple and grape juices. While the samples differed markedly in this respect, the outstanding effect of carbon treatment was in every case a very considerable lightening of color. In very heavily pigmented red or purple grape juices this effect is not highly objectionable, but in juices made from white or light-red grapes and in apple juices the use of carbon produces very light straw-colored liquids, quite unrecognizable as to source. Since the available carbons of vegetable origin had been subjected to special treatments specifically designed to increase decolorizing power, as Zerban (*34*) has pointed out, this result was to be anticipated in so far as such special carbons are concerned, but the effect of boneblack upon the color of the lighter juices was also so pronounced as to make its use inadvisable except with very deeply colored juices.

(3) All the carbons employed have a perceptible effect upon flavor. In the case of some highly flavored, strongly foxy or musky juices, this effect, while perceptible, is not undesirable, but in delicately flavored grape juices and in apple juices it detracts materially from the beverage quality of the product. The alteration is due in most part to the adsorption of tannin and in less degree to the removal of acids by the carbon, as is shown by the decided improvement in flavor produced by restoring these constituents in amounts equal to those removed. But other unknown constituents which play a part in determining the characteristic flavors of the several juices are also removed. This is shown by the fact that juices "reconstituted" by additions of acid and tannin are always readily distinguished by taste even by inexperienced persons from untreated samples of the same variety. Treatment of the carbon prior to use by washing with a dilute solution of tannic acid in malic or tartaric acid reduced the effect in so far as these constituents are concerned, but it did not prevent perceptible alterations in flavor. La Marca (*16*) in his work upon the clarification of wines, found that the use of carbon reduced acidity, tannin content, and extractives, and Gore (*14*) has stated that when orange or lemon juices are treated with carbon "it is advantageous to add orange or lemon flavor, in the respective cases, to the respective juices prior to sterilization, in order to restore their

distinctive flavor." The results obtained by the Bureau of Plant Industry with a large number of apple and grape juices indicate that carbon has too much effect upon flavor to permit its use with apple juices or with any but the more strongly flavored grape juices.

(4) The various carbons differ materially in the degree of transparency which it is possible to produce in a given juice by their use. In part, these differences are due to differences in adsorbing surface presented by equal weights of material ground to unequal degrees of fineness, but in part they are specific differences due to differences in porosity, in ash content, or to other factors not controllable by separation of the samples into particles of like size by screening. The results indicate that the character and amount of ash in a given carbon may have considerable significance in determining the efficiency of the carbon in the removal of colloidal material of the nature here dealt with, namely, pectins and gums. A certain sample of animal charcoal, when prepared for use in the usual manner by treatment with hydrochloric acid and washing free of acid with water (*20*, p. 22; *31*, p. 88), gave a clearer, more brilliant product than any other carbon. When this charcoal was subjected to exhaustive treatment in order to remove salts as completely as possible, its clarifying efficiency was reduced practically to the level of other carbons. This, of course, suggested that it may be possible to improve the efficiency of carbons for the particular purpose here aimed at by preliminary chemical treatment, but the fact that carbons are not well adapted to the purpose in other respects made it appear inadvisable to follow up the suggestion, especially since Zerban and his associates (*34*, *36*, *37*) already have under investigation the broader problem of the particular property or constituent of carbons which gives them clarifying power.

(5) The removal of pectins and gums by carbon is very incomplete in the case of apple and grape juices, as Zerban (*34*) has shown to be the case in cane juices. Consequently, the pasteurization of juices clarified with carbon is followed by the formation of a considerable precipitate unless such juices have been subjected to preliminary pasteurization followed by the removal of the heat-coagulable material prior to treatment with carbon. This double pasteurization is to be avoided if possible, as it materially increases the labor and cost of handling, while at the same time increasing the loss of flavor.

(6) Considerable difficulty is encountered in dealing with viscous juices after the addition of carbon, even when subjected to preliminary pasteurization, as a result of the fact that a portion of the added carbon forms a persistent suspension in the liquid. This can not be removed by any of the usual methods of filtration, and when juices so treated are pasteurized and stored there is a slow deposition of carbon upon the sides and bottom of the containers. Gore (*14*) encountered this difficulty and found it necessary to add diatomaceous ("infusorial") earth and to filter in order to remove the carbon. His process as applied to the more difficult juices consequently involved a preliminary treatment with infusorial earth and filtration, treatment with carbon, a second treatment with earth, and a second filtration. As some time must be allowed to permit sedimentation after each step in the treatment, the process is laborious and requires rather careful temperature control to prevent fermentation. The repeated handling necessarily involves a greater danger of infection with mold spores and increases the difficulty of securing perfect pasteurization.

In view of the many serious difficulties encountered in the use of carbon and the decided denaturing effects upon color and flavor of all but the most strongly flavored and deeply colored juices, it

appears that such carbons as have been studied must be regarded as decolorizing agents rather than as potentially valuable aids in clarifying fruit juices.

GELATINOUS SILICA AS A CLARIFYING AGENT.

Deprax (*9*), in a brief popular note, has reported good results in the clarification of beers which had proved refractory to the usual fining with gelatin from the use of "gelatinous silica" prepared by precipitating an aqueous solution of an alkaline silicate by adding HCl or H_2SO_4, washing, filtering, and pressing. Though it is noted that certain conditions of concentration must be observed, these are not stated. The author also suggests that the process may be greatly simplified by the substitution of ammonia or ammoniacal salts for acids as precipitating agents, stating that the resulting mixture is as effective for clarifying purposes as the acid precipitate. Using 100 grams of the gel, containing 17 grams of dry silicic acid per hectoliter of beer, he reports that he obtains a relatively dense, rapidly formed, quick-settling precipitate. In exceptional cases, larger quantities are necessary, but Deprax states that large quantities might be used, since he has determined that the material is insoluble in the liquid.

An extensive literature has grown out of Martin's discovery (*19*) that colloids may be removed from their dispersion means by filtration through a suitably supported layer of silicic-acid gel, and every textbook of colloid chemistry devotes considerable space to ultrafiltration through this and similar gels as a means to this end. Little attention seems to have been given to the possibility of the use of silicic-acid gel as an adsorbing agent in the manner suggested by Deprax, and his note is the only record that it has been possible to find in the literature of an attempt to use it as a clarifying agent for beer or wine.

Deprax (*9*) gives no details as to the preparation of his material; it is clear, however, that when sodium or potassium silicate was treated with HCl or H_2SO_4, the precipitate consisted mainly of metasilicic acid, H_2SiO_3, with some orthosilicic acid, H_4SiO_4, containing sulphates or chlorids of sodium or potassium. When ammonium salts or NH_4OH were employed as precipitants, the resulting mixture of silicic acids contained sodium and potassium salts or hydroxids together with free ammonia. Since Deprax prepared his material by washing, filtering, and pressing, it is certain that all these impurities were present in the respective preparations.

In the work done in the laboratory of the Bureau of Plant Industry it has been found impossible to produce satisfactory clarification with silicic-acid gels. Such crude preparations as Deprax em-

ployed retain traces of salts even after very prolonged washing on a filter and can be purified only by dialysis. A portion of the material forms quite stable suspension in a fruit juice to which it is added, the precipitate forms very slowly, the removal of colloidal matter is imperfect, and the filtration of a juice so treated is almost impossible by reason of the prompt formation over the filtering surface of a slimy, well-nigh impervious layer. Silicic-acid gels prepared and purified by more exact methods also fail to give satisfactory clarification or to filter readily. The preparation of the gel involves too many difficulties, and its use yields results too far short of satisfaction to make it a promising material for use in clarifying fruit juices.

DIATOMACEOUS EARTH (KIESELGUHR) AS A CLARIFYING AGENT.

Diatomaceous ("infusorial") earth (kieselguhr)[2] has been recommended as a filtering agent for various liquids, and patents covering its use in clarifying cane juices were issued in both Great Britain and the United States as early as 1886 (*21*, p. 586). Its use for the purpose, either alone or in combination with other materials, has been repeatedly suggested in the older literature. More recently there has been a decided revival of interest in kieselguhr as a clarifying agent, as evidenced by a considerable number of papers and the patenting of several processes. Gore (*12*) recommended its use as an aid to the filtration of previously neutralized apple juice in making apple sirup and also as an aid in filtering fresh apple juices through a filter press (*13*). More recently Peck and Adams (*26*) have described a new carbon intended for use in clarifying cane juices, which is made by mixing molasses with kieselguhr, treating with sulphuric acid, baking, and washing free of acid. The material is reported to have very great decolorizing power and to give very considerable increase in purity with a reduction of gums to 30 to 45 per cent of the amounts present before treatment, which would suggest, in view of Zerban's results with carbons, that the kieselguhr aids very materially in the adsorption of gums.

Peck (*24*) has reported results obtained by the addition of kieselguhr to the juice at the rate of 5 pounds per ton of cane, with considerable increase in purity. The same author in an address has also made incidental mention (*25*) of the work of Walter L. Jordan in filtering juices through kieselguhr, stating that an increase in purity was obtained, but Peck gives neither details nor citation of Jordan's paper, which it has been impossible to locate in the litera-

[2] Since kieselguhr consists chiefly or wholly of the siliceous frustules of diatoms, it is unfortunate that the older and correct designations diatomaceous earth, diatomite, or tripolite, which suggest the origin and chemical character of the material, should have been replaced in trade usage by the wholly misleading term "infusorial earth."

ture. Norris and McAllep (*22*) have published a note on the use of diatomaceous earth as an aid to the filtration of small quantities of raw cane juice in the laboratory, using brass wire screen beneath the filter paper in a Buchner funnel. Heriot (*15*, p. 205–206) describes a method of employing kieselguhr on a factory scale in filtering cane juice. Zerban (*35*), whose paper cites a number of papers from the older literature on the use of kieselguhr, has reported the results of both laboratory and factory scale tests of a specially prepared diatomaceous earth, which was used in filtration of cane juice preparatory to filtering through carbon, with excellent results. Wooster (*33*) has patented a process of filtering raw cane juice which appears to be essentially identical with those of Peck (*25*) and Zerban (*35*), since it consists in the addition to the raw juice of kieselguhr and filtration through filter presses. Martel (*18*) has designed a leaf filter which is said to be highly effective in clarifying cane juice. The juice, as it comes from the mill, is mixed with specially prepared diatomaceous earth, agitated, heated nearly to boiling point, and forced into the filters at low pressure—30 pounds per square foot. Dale and Hudson (*8*) have described a process of clarification for use with sugar-cane juice in sirup manufacture, the juice being heated to boiling, mixed with diatomaceous earth at the rate of 5 to 6 pounds per hundred gallons, and immediately pumped through a plate-and-frame filter press. With smaller quantities of the earth, filtration was retarded by the formation of a slimy, almost impervious coating on the filter cloths. The method gave a better clarification than it was possible to obtain by the usual methods of straining and skimming, and the resulting sirup was considered superior in flavor to the usual commercial product. Coates (*6*) has reported satisfactory results from the use of diatomaceous earth at the rate of 12 to 16 pounds per ton in the filtration of tropical raw sugars in Louisiana sugar factories, the earth, previously made to a thin cream with water, being added to the sugar prior to melting.

Paine and Walton (*23*) have recently presented before the sugar section of the American Chemical Society a report of a comparative study of various diatomaceous earths with reference to their clarifying efficiency for cane juices, finding that considerable differences in physical properties do not materially affect the values of the various earths for this purpose.

Chace (*5*) has reported experiments upon grapefruit juices, in which satisfactory clarification is obtained by pasteurizing the freshly expressed juice, storing until sedimentation is completed, decanting, mixing with kieselguhr, filtering through cloth, bottling, and pasteurizing. Cruess (*7*) mentions the fact that diatomaceous earth may be used as an aid to the filtration of grape juices and

loganberry (Logan blackberry) juices, adding that it may affect flavor. As this author states elsewhere in the same publication that egg albumen, casein, and Spanish clay are the clarifying agents which have been found most satisfactory for use with fruit juices in his laboratory, he evidently did not consider that diatomaceous earth had possibilities for the purpose.

Wilson (*32*) in a very recent paper outlining the method of manufacture of citric acid from lemons, states that prepared diatomaceous earth is added to the raw juice, the liquid then being heated to boiling and passed hot through the filter press, which is said to deliver "a brilliant amber-colored juice."

EXPERIMENTS WITH DIATOMACEOUS EARTH FOR CLARIFYING FRUIT JUICES.

The writer's experimental work with diatomaceous earth was begun in the autumn of 1918, prior to the publication of the group of recent papers just cited and without knowledge of the work under way in the various laboratories from which they came. It was suggested, however, by such references to the use of diatomaceous earth in the clarification of cane juices as are found in the older standard handbooks on sugar manufacture. The possibilities of a material combining insolubility, a high degree of freedom from contaminating foreign matter, and immense absorbing surface were immediately obvious, and various samples of diatomaceous earth, of both American and foreign origin, were obtained for use in preliminary experiments. In these tests a relatively small number of apple and grape juices, selected so that they might fairly represent the range of variation in color and in physical characters found in these juices, were employed. All the tests in 1918 were made upon juices previously pasteurized and stored until sedimentation had ceased, but all were opaque, turbid solutions.

It was immediately apparent that diatomaceous earth combined excellent clarifying power with very slight or insignificant effect upon the coloring matter of apple and grape juices. In every case the effect of treatment with the earth was an apparent deepening of the color of the liquid due to its transparency after removal of the colloidal material, so that visitors to the laboratory refused to believe that treated juices had not been artificially colored. There was noticeable in all the more delicately flavored juices a peculiar alteration in taste, described by some as an "earthy" flavor, by others as a "rancid, old-butterlike" taste. This was more marked in samples treated with one of the lots of diatomaceous earth than in others but was perceptible in all. It was attributed to the presence of a soluble impurity in the earth. The fact that living diatoms contain amounts

of wax varying between 5 and 50 per cent by weight,[3] the relation of certain commercially employed upper Miocene deposits of diatomaceous earth to oil fields (*1*, *2*), and the character of the flavor imparted to juices indicated that the material might be a derivative of wax. This assumption was borne out by its behavior, but no attempt to isolate the material in quantity or to study it chemically was made. Attention was directed to the working out of simple methods for removing it with sufficient completeness to make the earth free from discoverable effect upon the flavor of the juices.

PURIFICATION OF THE EARTH.

Extraction of the earth with the usual fat solvents completely removed the material which gives foreign flavor to juices, but such treatment on other than an experimental scale is impracticable. Attempts to wash out the contaminating material in the manner recommended by some filter-press manufacturers, by stirring the earth into boiling water, decanting after settling, and repeating the process a few times, proved ineffective, as earth so treated still had perceptible effect upon the flavor of delicate juices after 10 or 12 changes of water. Earth boiled on a water bath for several days with repeated changes of water was not wholly freed of the contaminating material.

The most satisfactory method of purifying the earth was by incineration. In preliminary work small lots were placed in porcelain dishes, heated to low redness for 30 minutes in an electric furnace, allowed to cool, and rubbed through a sieve having 50 to 80 meshes per inch. For the preparation of larger lots a metal container made by capping one end of a 4-inch iron pipe 20 inches long and providing a loosely fitting plug for the opposite end was used. This was filled with the earth, plugged, placed in the fire box of a steam boiler, and allowed to remain for an hour. An ordinary heavy-walled steel kettle provided with a lid has also been used with satisfactory results. The traces of iron thus added to the earth are without discoverable effect upon the juices.

Purification by heating has the obvious advantage that it permits repeated use of the earth. On burning a quantity of earth which has become loaded with material derived from the juice an insignificant amount of ash remains in the earth, but this does not materially increase with repeated use. Carbon progressively accumulates with repeated burnings, ultimately becoming sufficient to exert an appreciable decolorizing effect upon juices filtered through it. In practice it has been found possible to use a single lot of earth 10 to 15 times, revivifying by burning after each use, before the carbon

[3] Mann, Albert. Personal communication to the writer.

present begins to affect the color of the juices, and even after such prolonged use the earth may give considerable further service in treating heavily colored juices.

DIFFICULTIES ENCOUNTERED IN FILTERING TREATED JUICES.

In the earier work various treatments were employed in the attempt to devise satisfactory methods of filtration after treatment with the earth which would be usable on a small scale. Some difficulty in obtaining a perfectly transparent filtrate arises from the fact that diatomaceous earth contains a considerable quantity of excessively fine fragments of broken frustules which pass through ordinary filters and later partially settle out upon the walls of the containers. Lenher (*17*) has shown that when silica or orthoclase is ground until most of the particles are less than 0.004 mm. in diameter, shaken up in water, and allowed to stand for several weeks the larger portion of the suspended material settles quickly, but the finer particles form strata in the liquid which persist for 10 days. At the end of 15 days the solution is stable, but a portion of the material is in colloidal solution and shows Brownian movement and Tyndall effect. It is clear from results obtained in the laboratory that analogous conditions result when diatomaceous earth containing minute fragments of broken frustules is added to a fruit juice, as a progressive settling extending over some days or weeks occurs when a sample of treated juice which has been filtered through paper is allowed to stand undisturbed.

As the centrifuge is successfully used in a wide variety of otherwise difficult separations and has repeatedly been suggested as a substitute for filtration in the clearing of fruit juices (*11*), its possibilities as a means for clarifying ciders treated with diatomaceous earth were thoroughly tested. After being thoroughly mixed with the earth, the juices were repeatedly passed through a gear-driven laboratory supercentrifuge having a maximum speed of 25,000 revolutions per minute. A single passage through the machine was practically as effective as three or more, since only a very small trace of material was recovered by any treatment after the first. While the appearance of treated juices was greatly improved, a considerable amount of colloidal material remained in suspension even after repeated stirring with earth followed by passage through the centrifuge. Juices so treated and subsequently pasteurized and stored remained for 18 months as hazy colloidal solutions. Attempts further to clarify such centrifuged juices by ordinary filtration were unsuccessful, as any filter having sufficiently close texture to hold back the suspended particles quickly became choked by slime.

For these reasons the complete removal of the added earth from the juices by any of the more generally available methods of filtration appeared somewhat difficult at the outset. The best types of

plate-and-frame filter presses handle such filtration problems successfully, but the cost of such equipment limits its use to commercial-size installations. A pulp filter operated by a steam suction pump failed to give satisfactory results. When first started, such a filter permits the passage of particles of earth; by the time this ceases the surface of the pulp has become coated with a slimy, almost impervious layer, and filtration becomes extremely slow. Increasing the suction upon the filter merely hastens clogging by making this slimy layer more compact. Attempts to use a small multiple-disk pulp filter fed by gravity were equally unsuccessful; clogging and stoppage occurred very quickly under gravity pressures ranging from one-fourth to two atmospheres. The difficulty with such filters is twofold. The filtering medium is not sufficiently close in texture to retain the finer particles until it has become reinforced by a layer of earth. As the earth settles out of the undisturbed liquid, the larger and heavier particles come down first, followed by the deposition of successive strata of finer and finer particles. Such a layer of earth is a highly efficient filtering medium in so far as preventing the passage of suspended material is concerned, but its working period is short, for the reason that there is soon built up on the surface a layer of gummy, viscous material which practically stops the flow and necessitates cleaning and repacking the filter. No satisfactory method of overcoming this twofold difficulty in the use of pulp filters either of the gravity or of the suction type has been found.

SIMPLE AND EFFECTIVE METHODS OF FILTRATION WITH DIATOMACEOUS EARTH.

SMALL MULTIPLE-DISK FILTER.

As a plate-and-frame type of filter press was not available in the laboratory, a small multiple-disk pulp filter was so modified as to make it essentially a plate-and-frame filter. The circular pulp disks were replaced by filter cloths of a closely woven, rather light denim, fastened in place at the outer edge and around the central opening by rubber gaskets. When all were in place the press was closed and water was passed through to wet the cloths thoroughly. A quantity of earth sufficient to coat the cloths to a depth of about 0.5 cm. was then thoroughly stirred into water and passed into the press. As the filter was of the vertical type in which the disks rest one upon another like a pile of coins, it was easy to effect uniform distribution of the earth over the cloths by running it in while in suspension in water under a head of 6 to 10 feet. Water was then passed in until earth ceased to wash through. The juice to be filtered was then stirred thoroughly with diatomaceous earth at the rate of two-thirds to 1 ounce per gallon (4 to 6 pounds per hundred gallons) and passed into

the filter from a feed tank with a gravity head of 10 to 12 feet. The juice in the feed tank was vigorously stirred from time to time to maintain a uniform suspension and prevent the clogging of the feed line. The filtrate was clear and brilliant; filtration was quite rapid and was maintained at an almost uniform rate until the press had become completely filled with quite compact cakes. As the filter was not so constructed as to permit thorough cleaning by back flushing, it was necessary to open the press to clean it, but the cakes could be turned off the cloths practically entire, the cloths washed and replaced, and the press made ready for a second run in considerably less time than was required to clean and repack the same press with filter pulp.

SUGGESTIONS FOR THE MANUFACTURE OF A SMALL FILTER.

If the makers of filtering equipment would devote some attention to the manufacture of filtering devices suited to use with diatomaceous earth which would have the efficiency of some of the small laboratory filters now made for experimental use, placing them on the market in a range of sizes and at prices which would put them within reach of fruit growers and small operators who make a few hundred to a few thousand gallons of cider or grape juice annually, they should find a very considerable market. Such filters might be of any one of several types. A wooden plate-and-frame press to be fed either by a pump or under a gravity pressure of 12 to 15 pounds, so constructed as to permit cleaning by back flushing, should give satisfactory results. The vertical multiple-disk filter, consisting of a series of superposed metal plates each carrying a disk of filter pulp, if modified so as to permit the substitution for pulp of readily attached filter cloths and to provide for the removal of the cake by back flushing with water, should also be efficient, as the vertical position of the filter areas facilitates deposition of a uniform film of earth over them and secures uniform cakes free from channels. A further advantageous modification of this type would be the deepening of the chambers so as to give space for thicker cakes. Such a filter might be operated either by gravity or by a pump.

The leaf filter has a number of features which lend themselves very advantageously to the filtration of fruit juices and which make it possible to construct inexpensive filters of small capacity. The leaf type of construction makes it possible to obtain a large filtering area in a small apparatus, while the fact that filtration is from without inward permits the quick cleaning of the filter cloths as they become clogged without removing them from the frames. Such a filter might be made up in units of two or more leaves, to be installed by the user in any suitable tank and operated either by suction or by gravity, at very moderate cost.

SIMPLE METHODS FOR USE WITHOUT SPECIAL EQUIPMENT.

In the absence on the market of any suitable small-capacity press adapted to the handling of juices with diatomaceous earth, some time was devoted to the working out of methods by which the small operator without special equipment could avail himself of the advantages offered by the use of earth. The purpose in view was to devise an arrangement in which filtration would occur through a layer of earth which could be kept from clogging. Clogging can be effectively prevented by keeping the mixture of earth and liquid thoroughly agitated, thus securing the constant renewal of the filtering surface by deposition of the solid particles of earth in mixture with the amorphous suspended material of the juice. Without such provision for agitation the larger particles of earth would quickly come down, after which clogging by the amorphous slimy matter arrested at the surface would soon occur. It was necessary also to make provision for the easy and quick cleaning of the filter or the renewal of the filtering layer.

A LABORATORY FILTER.

A very simple arrangement meeting these requirements and using a compact layer of earth as a filtering medium has been in use in this laboratory for some time. It yields a permanently clear filtrate at a satisfactory rate and is readily cleaned when necessary. In the first small filter made for use in the laboratory, a piece of 100-mesh nickel-wire gauze was cut to fit as closely as possible into a large Buchner funnel. A quantity of diatomaceous earth was made up into a thick paste with water, spread upon the gauze in a layer 2 to 3 cm. thick, packed under gentle suction, and washed with water until earth ceased to come through, care being taken to keep the surface of the layer of earth as smooth as possible. Filtration was then begun. The juice to be filtered was mixed with diatomaceous earth, stirred thoroughly, and immediately poured on the filter. Care was taken to repeat the stirring of the liquid every time the filter was refilled. When the formation of a layer of slime over the surface materially reduces the rate of filtration, the filter is allowed to empty itself, a thin film of earth carrying with it the gummy deposit is removed with a spatula or similar instrument and stored for revivification by burning, and filtration is resumed. By making the layer of earth 2 to 3 cm. thick at the outset and packing it firmly, this treatment can be repeated almost indefinitely, as the material which causes clogging is practically wholly arrested at the surface, penetrating at most only a millimeter or two into a properly packed disk.

A FILTER FOR USE ON A SEMICOMMERCIAL SCALE.

A similar arrangement for use on a larger or semicommercial scale was made from a pulp filter operated by a steam suction pump by removing the pulp packing and replacing it with a heavy nickel-wire screen fastened permanently in place. Upon this as a support was placed a piece of heavy closely woven denim. Diatomaceous earth in the form of a thick paste was then poured in and packed into a firm disk about 3 to 3½ cm. thick by gentle suction and pressing down with a wooden rammer. A few minutes' washing with water under full suction removed all traces of earth from the lower surface of the cloth. Such an arrangement filters rapidly, can be restored to the original rate of filtration when partial clogging occurs by scraping off the accumulated slime together with a thin layer of the compact disk, and when necessary can be taken out and replaced in a very short time. In setting up and operating such a filter it is necessary to observe a few rather obvious precautions. The wire screen used as a support should be of a metal which is not attacked by the acids of the juice, though in default of a satisfactory screen a wooden lattice may be used. Whatever the material used, the support must be rigid, in order that the filter disk may not be displaced or broken by starting or stopping the suction pump. The cloth used as a backing should be of firm closely woven texture, in order that particles of the earth may not wash through it into the filtrate, and should be thoroughly wetted before it is put into place. The earth used in packing the filter should be made into a paste with as little water as possible, as it then holds together like putty, does not pass through the cloth, and can readily be molded into a uniform layer, making close contact with the side walls of the container. When the earth is so packed very little washing is necessary. In filling the filter with juice, care must be taken not to allow the entering stream to strike the disk with sufficient force to wash holes in it. The liquid on the filter should be thoroughly stirred from time to time. Care must be taken not to allow the disk to become dry, as the earth then shrinks considerably and will crack and pull away from the side walls of the container if not kept thoroughly moist. In cleaning the surface of the filter when it becomes coated with slime, a broad-bladed putty knife or some similar instrument which permits the operator to pare off a uniform thin layer from the top of the disk should be employed. When the removal of the disk is necessary it should be allowed to become rather dry; it may then be lifted out practically entire. The cloth used as a backing should be taken out and thoroughly washed before the filter is replaced. The disks which have become clogged from use, together

with the material accumulated by scraping the filter, are preserved and burned for subsequent use.

It will be seen from the foregoing description that this arrangement gives essentially the advantages obtained by the use of molded silica filtering plates, with the differences that the material used is inexpensive and may be used over and over again practically without loss; that there is no danger from breakage, as in the case of filter plates; that cleaning and replacement are matters of a few minutes' work only; and that the filtering disks may be made of any size or shape desired by the individual operator, who may readily make one or more filters of any desired capacity to suit his needs.

A FILTER FOR HOUSEHOLD USE.

For handling small quantities of juice, such as would be put up for individual household use, where a suction pump is not available, very satisfactory results are obtained by gravity filtration through a disk of earth. The vessel used should be a deep one, in order that the column of liquid upon the filter may be heavy enough to aid filtration; for this reason also the vessel should be kept full while filtration is going on. A cask provided with a false bottom for supporting the filter and a faucet placed just below it for drawing off the juice serves very well. The filter disk should be made somewhat thicker than would be the case in a filter operated by suction and greater care must be employed to pack the earth firmly over the whole surface and especially along the walls of the container. Caution must be employed in filling the filter for the first time, in order not to wash holes in the layer of earth; it is well to place a wooden float in the vessel and to pour the juice upon it, as the disk of a gravity filter, unlike that of a suction filter, becomes less rather than more compact in use. For this reason there is less choking, and a gravity filter under a head of 2 feet of liquid will run at a practically uniform rate for a long period, as there is much less tendency to form a compact slime layer over the surface than when suction is used.

A FILTER OF THE JELLY-BAG TYPE.

A device of the jelly-bag type permits quite satisfactory filtration of small quantities which would not justify the making of a more elaborate filter. The bag should be made of heavy closely woven denim and should have the form of a rather tall cone. The seam should be double and should preferably be made by machine in order to guard against leakage. After wetting the bag thoroughly, it should be suspended and such a quantity of earth, previously made into a thin paste with water, poured into it as will practically fill it. After the water has drained away the treatment should be repeated,

if necessary, in order to cover the entire inner surface of the bag with an adhering layer of earth, after which water is passed through until the outer surface is washed free of the earth. The filter is then ready for use. It is well to keep the bag practically full to the top, not only in order that the entire filtering surface may be used, but also because of the more rapid filtration per unit area resulting from the greater weight on the surface. While satisfactory clarification is obtained with such an arrangement, its use should be confined to the handling of very small quantities.

PASTEURIZING BEFORE FILTERING.

In the earlier experiments with diatomaceous earth, in the seasons of 1918 and 1919, the juices employed were in all cases pasteurized immediately after pressing and were subsequently stored until the settling out of cellular débris and heat-coagulable material had become fairly complete before attempts to clarify them were made. The length of the storage period was determined by convenience and the pressure of other work, ranging from four weeks to nine months as extremes. Sedimentation was usually complete at the end of three weeks in the storage room, which was a room in the laboratory building with no means of temperature control other than a steam coil to prevent freezing in severe weather.

In some cases the juice, after being decanted from the sediment in the containers, was placed in a large vessel, thoroughly mixed with the earth by prolonged stirring, and allowed to remain undisturbed for several hours or overnight. It was then decanted with as little disturbance of the sediment as possible, mixed with a second smaller quantity of earth, and at once filtered. In other cases the juice was mixed with the earth, allowed to stand for 10 to 15 minutes with occasional stirring, and filtered without permitting settling to occur. As this treatment gave as satisfactory results as the other, all the juices dealt with in the later work were filtered as soon as convenient after being mixed with the earth.

Juices treated in this manner were brilliantly clear and remained transparent after being bottled, pasteurized, and stored for more than 12 months in a laboratory room subject to wide fluctuations of temperature. The characteristic flavors of juices so treated are not injuriously affected.

FILTRATION OF FRESHLY PRESSED JUICES.

Success in the treatment of juices which had previously been pasteurized and stored led to the hope that it might be possible to apply the treatment to freshly expressed juices, thus dispensing with storage and making the whole process of preserving fruit juices a continuous one, in which pressing should be followed immediately by

filtration and then by pasteurization in the final containers. A few preliminary experiments in the season of 1919 gave some encouragement to this idea, which was fairly thoroughly tested in the autumn of 1920. Several methods of handling the juices were employed. These will be outlined and their advantages and disadvantages indicated.

TREATMENT WITH EARTH, FOLLOWED BY SEDIMENTATION, BEFORE FILTERING.

In order to ascertain whether mixing with diatomaceous earth, sedimentation, and decantation prior to filtration would be advantageous, a quantity of juice was divided into three lots. One of these was strained through cotton cloth, to remove fragments of pulp as completely as possible, and was then thoroughly mixed with the earth at the rate of 1 ounce of earth per gallon (6 pounds per hundred gallons). The second portion received an equal quantity of earth but was not previously strained to remove the pulp. The third lot was neither strained nor mixed with earth. The three lots were then placed in 5-gallon carboys, which were filled to the neck, corked, and placed in a basement room at a temperature of 55° F. for 18 hours, to allow sedimentation to occur. At the end of this time the lot which had received no treatment showed a fairly compact precipitate about 2 inches thick at the bottom of a 5-gallon carboy; the other two lots showed compact deposits 3 to 3½ inches thick, above which was a zone of less closely aggregated material, followed by poorly defined zones, each containing less suspended material than the next below. In this respect the lot which had been strained through cloth showed little, if any, difference from the unstrained lot. On carefully siphoning off the liquid it was possible to draw off 4⅝ gallons from the untreated carboy without greatly disturbing the sediment. Of the lots treated with earth, it was possible to draw off only 4¼ gallons from the lot which had been strained prior to the addition of earth, and 4⅛ gallons from that which had not been strained, before the liquid flowing from the siphon became very densely turbid from the drawing up of loosely aggregated material. There was consequently twice as much sludge in the case of treated juices, but it was of a very much less compact character.

Each of the three lots of juice was next treated with earth at the rate of 1 ounce per gallon, thoroughly stirred, and immediately filtered through a disk of earth with suction, the sludge from each lot being placed on the filter and drained as completely as possible after the siphoned liquid had passed through. A fresh filter disk was prepared for each lot, and uniform suction was employed throughout. The filtrates were equally brilliant. The juice which had not received a preliminary treatment with earth required about

10 per cent more time to pass through the filter, as a result of a greater tendency to clog the disk with slime, but gave a slightly greater yield of filtered juice than the others, since it was possible to reduce the sludge to a drier condition. The juices which had received the preliminary treatment filtered more quickly and with less clogging, but the bulky sludges could not be satisfactorily filtered dry.

In other experiments juices treated with earth were held for longer periods at lower temperatures, in order to prevent fermentation while allowing sedimentation to become complete. Here one encounters a difficulty arising out of the fact that as the temperature at which the juice is held is lowered, the viscosity of the liquid is increased, slowing down the rate of sedimentation and making it less complete.

A rather extended series of experiments has shown conclusively that the additional handling necessary and the greater loss of juice resulting from inability to filter the sludges satisfactorily make a preliminary treatment with earth followed by sedimentation before filtering inadvisable. A larger yield of filtered juice is obtained with a smaller expenditure of labor when the juice is allowed to stand undisturbed for 12 to 24 hours after pressing in order to allow the settling out of cellular débris, then decanted, mixed thoroughly with earth, and immediately filtered.

SEDIMENTATION BEFORE FILTERING.

A period of sedimentation before filtering is quite necessary and should never be omitted if an effort to obtain a perfectly permanent, clear, brilliant filtrate is being made. When either apple or grape juice is taken directly from the press, mixed with earth, and filtered, the liquid coming through the filter is perfectly transparent. On bottling and pasteurizing such juices and allowing them to stand for some time, however, cloudiness or haziness appears. The degree of the change varies greatly with various fruits, but all juices so treated become in some degree turbid colloidal solutions, while in some cases a deposit is ultimately formed in the bottles. Check samples of the same juices allowed to stand for 12 to 24 hours before treatment do not show this behavior, but remain permanently free from cloudiness or sediment.

The explanation of the facts just stated is not known, and only unproved hypotheses can be suggested. When the cells of the fruit are ruptured and the juice expressed and exposed to the air various constituents are brought together which were previously separated from one another in the cells but which are capable of reacting when brought into contact. The intercellular materials (pectin and its derivatives) are brought into contact with the acids of the juices and with pectase. It is conceivable that under such conditions a conversion of

the soluble pectin into a colloidal suspension may occur. Whatever the nature of the reaction, it is clear that it becomes complete within 24 hours at temperatures approximating 40° F., and in a shorter period at higher temperatures, becoming complete in a few minutes when juices are heated to the temperature of pasteurization. Consequently, if juices are held in the settling tank overnight, or for 24 hours if the temperature is low enough to prevent fermentation, and are then decanted, clarified, and bottled, no difficulty due to subsequent clouding of the liquid in the bottles will be encountered.

EXPEDIENTS TO SHORTEN THE PROCESS.

Various expedients have been resorted to in the course of the work in attempts to increase the ease of filtration or to shorten the process by permitting clarification and bottling immediately after pressing. Some of these gave negative results and are mentioned only in order that they may be avoided by others; some are advantageous if properly employed.

HEATING THE JUICE BEFORE FILTERING.

Heating the juice prior to filtration has many obvious advantages, chief among which are the precipitation of heat-coagulable constituents and the lowering of the viscosity of the liquid thereby produced. Hot filtration, however, is of very definitely limited applicability to fruit juices. It can be advantageously employed only for such juices as do not readily lose their characteristic flavors on heating and subsequent exposure to the air while hot. Such grape juices as those of Concord, Norton, Clinton, Clevener, Early Victor, Worden, Ives, Diogenes, Moore (*Moore's Early*), Cynthiana, Montefiore, and Niagara are not injured in quality or flavor by such treatment, which makes possible the usual commercial practice of crushing the grapes and heating to 175° F. in kettles prior to pressing. With all of these varieties excellent results are obtained by hot filtration. If the grapes are heated before pressing, the hot juice is taken directly from the press, thoroughly mixed with the earth, and immediately passed through the filter. If the grapes are pressed cold, the juice is at once heated to 165° to 175° F., mixed with the earth, and filtered. The juice obtained from any given variety by pressing cold is, of course, quite different from that obtained from heated grapes, but such juices are not injuriously affected by subsequent heating and hot filtration.

This method of treatment can not be employed with apple juice or with the more delicately flavored grape juices without considerable loss in quality. Juices of such varieties of grapes as Agawam, Brighton, Barry, Catawba, Delaware, Diana, Goethe, Elvira, Eumelan, Isabella, Lady, Massasoit, Missouri Riesling, Noah, Salem,

Rommel, Wilder, and Woodruff show material alteration in flavor after heating to 175° F. and filtering. There is also perceptible alteration in the flavor of apple juice, irrespective of variety, when so treated. The alteration in flavor is apparently identical with that which occurs when such juices are heated to pasteurizing temperatures in open vessels and is undoubtedly due to the loss of volatile constituents from the hot liquid during the unavoidable exposure to the air which occurs during filtering.

Experiments designed to determine the degree to which the heating of apple juices and the more easily injured grape juices may be carried without noticeable loss of characteristic flavor and quality indicate that the danger line for such juices lies between 130° and 140° F., when the liquid is slowly raised to this temperature in a tank heated by a steam coil or by placing it in open vessels sunk nearly to the top in a water bath. Juices heated to 130° F. in this manner, mixed with earth, and filtered hot showed no alteration in flavor. When heated to 140° F. and filtered while hot, such apple juices as those of York Imperial, Northern Spy, and Grimes, and such grape juices as those of Delaware, Isabella, Missouri Riesling, and Rommel were not perceptibly changed in flavor, while with such apple juices as those of Delicious and Winesap and such grape juices as Catawba, Goethe, Salem, Brilliant, and Brighton there was a distinct diminution in flavor. In the case of all these juices there was quite marked alteration in flavor in the lots heated to 150° F. before filtering, and the effect became more pronounced with the increase of the time during which the samples were kept at this temperature.

For these reasons, heating as an aid to filtration can be recommended only in cases in which the temperature can be rather closely controlled, and in no case should it be allowed to rise above 130° to 140° F. or to remain at this temperature more than a minute or two. Heating to these temperatures is insufficient to cause precipitation of the heat-coagulable material present in the juice, but very considerably increases the rate of filtration by diminishing the viscosity of the juice.

EXPERIMENTS WITH GRAPEFRUIT JUICES.

In the work with grapefruit juices reported by Chace (*5*), the juices were pressed, pasteurized, stored for some weeks until sedimentation had become fairly complete, decanted, mixed with diatomaceous earth, filtered, bottled, and pasteurized. It occurred to the writer that it might be possible to eliminate the preliminary pasteurization and subsequent period of storage in the case of grapefruit juice by applying to the freshly pressed juice the same methods found effective with apple and grape juices. This it has been possible to do.

Experiments with grapefruit juice were made at three periods in the life of the fruit, employing portions of the same lot of fruit. The first samples of juice were made on receipt of the fruit from the growers on November 9, the second on February 21, after the fruit had been in cold storage for 104 days, and the third on May 2, when the fruit had been in cold storage 174 days. The last lot of fruit had reached the limit of its life in storage and was in bad condition; pressing was difficult and the juice contained large quantities of pulp with a reduced yield, but clarification involved no difficulties. The treatment given the three lots was identical and the results were equally satisfactory; hence, an outline of one experiment only will be given.

The fruit was peeled, freed from adhering rag as completely as possible, passed through an apple grater, and pressed with a commercial hydraulic press. The juice was placed in deep containers and allowed to stand 18 hours for sedimentation to occur, after which it was decanted from the sediment. A portion was bottled and pasteurized, to serve for comparative purposes, and the remainder divided into portions of 10 gallons each. One of these was mixed with diatomaceous earth and at once passed through layers of earth supported on cloths in the disk filter press used in experiments with apple juice. The filtration was rather slow, but the product was entirely clear when bottled and pasteurized. The second lot was divided into two parts, one of which was mixed with earth, heated in an open vessel to 168° F., and filtered through freshly prepared earth filter plates in the same filter. This filtered more rapidly than the first lot, was equally clear, and showed no alteration in flavor. For purposes of comparison the remaining portion was heated to 168° F. without the addition of earth and filtered while hot through a closely packed pulp filter. As the filtrate was turbid and opaque, it was passed six times through the filter in an unsuccessful effort to improve its appearance. All the lots were then bottled and pasteurized in a hot-water tank at 168° F. for 30 minutes. Quart bottles of the untreated juice threw down a heavy precipitate upon standing and remained densely opaque after eight months' standing in a laboratory room. The juice filtered repeatedly through pulp while hot deposited a less heavy but considerable precipitate and held in suspension sufficient quantities of material to make the solution permanently opaque and tawny yellow in color. The juices filtered with the addition of diatomaceous earth, with or without subsequent heating prior to filtering, remained after eight months perfectly transparent and without a trace of precipitate, with a color suggesting that of olive oil and with a flavor indistinguishable from that of the untreated juice. It is consequently possible to shorten the process

of clarification and bottling with grapefruit juice by the employment of the same general methods found successful for apple and grape juices.

SUMMARY.

(1) The usual methods of filtration do not give satisfactory results when applied to unfermented apple, grape, and grapefruit juices, as such juices are difficult to filter and contain considerable quantities of colloidal material which pass through ordinary filters.

(2) Various methods of treatment designed to assist the clarification of these juices have been studied with a view to developing a means of making clear, transparent juices which would be applicable on a small scale.

(3) Clarification by means of enzyms can be accomplished, but the technical skill and the degree of control of conditions required in the work are such that the method is not adapted to general use in small-scale juice manufacture.

(4) The methods of clarification employed by wine makers, such as the addition of tannin and gelatin, casein, fish glue, egg albumen, and blood, should not be employed with unfermented apple and grape juices. Precipitation is slow and incomplete, the chemical composition of the juices is altered, and the palatability and flavor are decreased.

(5) Of the inert adsorbing agents used as aids in clarification, carbon is not suited for use with apple and grape juices. Carbons remove flavoring substances and have high decolorizing power and do not wholly remove pectins and gums. Carbon also forms persistent suspensions which pass through ordinary filters and ultimately deposit upon the sides of the container.

(6) The preparation of a suitable silicic-acid gel is tedious and difficult, the precipitation of colloidal material obtained by its use is imperfect and slow, and the filtration of juices so treated is difficult because of the prompt clogging of filters.

(7) Diatomaceous earth is by far the most satisfactory aid to the filtration of fruit juices yet employed. It is highly efficient in the removal of colloidal materials and does not remove coloring and flavoring substances.

(8) As obtained in the markets, diatomaceous earth contains varying amounts of wax derivatives which impart perceptible foreign flavors to most juices. These objectionable materials are readily removed by heating the earth to redness for a short time. Earth which has been used may be repeatedly "revivified" for further use by a similar treatment.

(9) Juices which are to be clarified by the use of diatomaceous earth should be allowed to stand undisturbed for 12 to 18 hours

after pressing, in order to permit the settling of cellular débris, and should then be siphoned or decanted from the sediment.

(10) The best results are obtained when the juices are thoroughly mixed with the diatomaceous earth at the rate of 6 to 8 pounds per 100 gallons and immediately filtered through a properly supported layer of the earth.

(11) During the filtration the juice on the filter should be thoroughly agitated occasionally, to keep the earth in suspension and prevent the sliming and choking of the filter.

(12) A number of filtering devices have been found satisfactory for use in filtering treated juices. The construction and operation of simple but effective filters adapted to use in home or semicommercial operations are described. Filters employing pulp are not suited to the purpose.

(13) Heating the liquid prior to mixing with the earth and filtering considerably increases the rate of filtration. If heating is conducted in open vessels or tanks, the temperature of the juice should not be allowed to exceed 130° to 140° F. and should not be long maintained at this temperature in the case of apple juices and the more delicately flavored grape juices or deterioration in flavor will occur. A few varieties of grapes yield juices which may be heated to 170° F. in open vessels without loss of flavor.

(14) Juices filtered with the aid of properly prepared diatomaceous earth on a suitable filter after previous sedimentation for 12 to 18 hours remain perfectly clear and transparent when bottled and pasteurized and retain the characteristic flavor and quality of the fresh juices in high degree.

(15) The employment of the methods of treatment herein described materially reduces the labor of preparing apple, grape, and grapefruit juices by eliminating preliminary pasteurization and storage in order to permit sedimentation, thus shortening the process of preparation and making it a continuous process. Losses from spoilage and breakage during this storage period are eliminated by making packing in the final containers possible; and a material improvement in the appearance of the product, together with a better preservation of flavor, is obtained.

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